Speciation of Heavy Metals - an important parameter for risk assessment of feed and food safety in aquaculture

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SPECIATION OF HEAVY METALS

– AN IMPORTANT PARAMETER FOR RISK ASSESSMENT OF FEED AND FOOD SAFETY IN AQUACULTURE

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Technical University of Denmark

DTU Food
National Food Institute
DTU




SEVENTH FRAMEWORK PROGRAMME

www.conffidence.eu

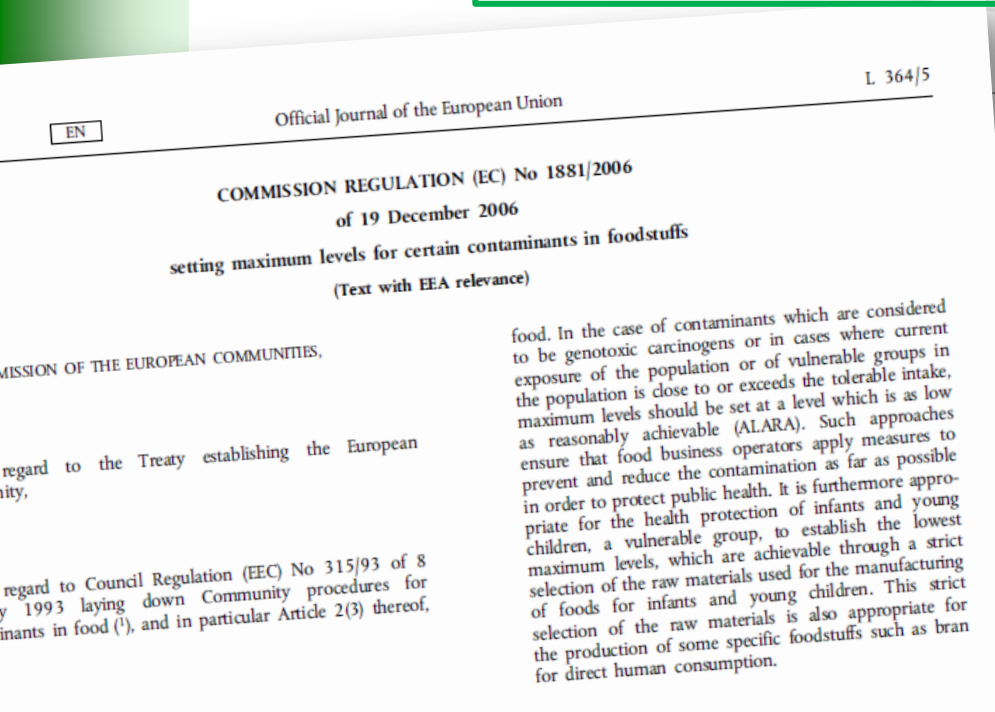
CONFFIDENCE

Current situation in EU legislation:

Foodstuffs
MLs for Pb, Cd, Hg and Sn
EU directive 2006/1881/EC

Animal feedingstuffs
MLs for As, Pb, Cd and Hg
EU directive 2002/32/EC

Only maximum levels for total concentration of the metals



EN Official Journal of the European Union L 364/5

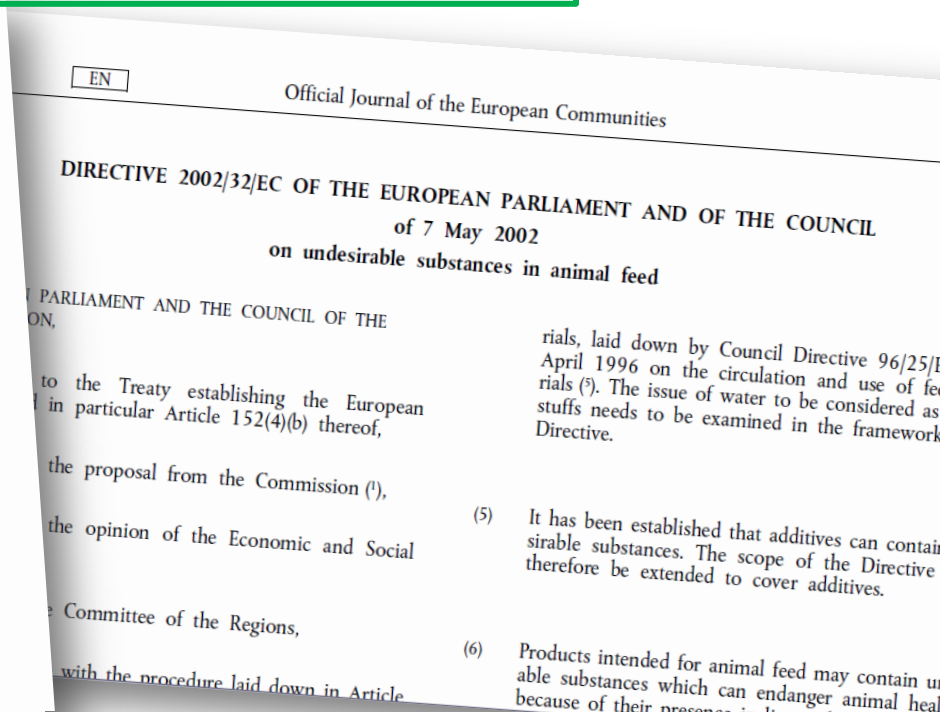
COMMISSION REGULATION (EC) No 1881/2006
of 19 December 2006
setting maximum levels for certain contaminants in foodstuffs
(Text with EEA relevance)

MISSION OF THE EUROPEAN COMMUNITIES,

regard to the Treaty establishing the European
nity,

regard to Council Regulation (EEC) No 315/93 of 8
y 1993 laying down Community procedures for
inants in food (1), and in particular Article 2(3) thereof,

food. In the case of contaminants which are considered to be genotoxic carcinogens or in cases where current exposure of the population or of vulnerable groups in the population is close to or exceeds the tolerable intake, maximum levels should be set at a level which is as low as reasonably achievable (ALARA). Such approaches ensure that food business operators apply measures to prevent and reduce the contamination as far as possible in order to protect public health. It is furthermore appropriate for the health protection of infants and young children, a vulnerable group, to establish the lowest maximum levels, which are achievable through a strict selection of the raw materials used for the manufacturing of foods for infants and young children. This strict selection of the raw materials is also appropriate for the production of some specific foodstuffs such as bran for direct human consumption.



EN Official Journal of the European Communities

DIRECTIVE 2002/32/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 7 May 2002
on undesirable substances in animal feed

PARLIAMENT AND THE COUNCIL OF THE
ON,

to the Treaty establishing the European
in particular Article 152(4)(b) thereof,

the proposal from the Commission (1),

the opinion of the Economic and Social

Committee of the Regions,

with the procedure laid down in Article

rials, laid down by Council Directive 96/25/E
April 1996 on the circulation and use of fe
rials (3). The issue of water to be considered as
stuffs needs to be examined in the framework
Directive.

(5) It has been established that additives can contain
sirable substances. The scope of the Directive
therefore be extended to cover additives.

(6) Products intended for animal feed may contain u
able substances which can endanger animal hea
because of their

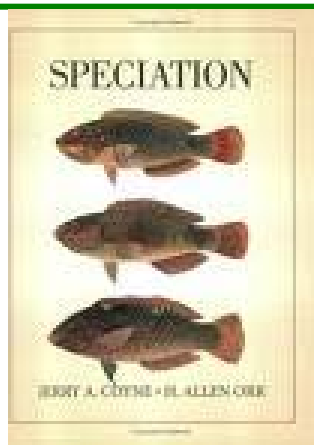
Speciation of elements

Information needed on

- biological activity
- toxicity

Total amount not always enough
Speciation analysis is required

- lifetime, fate and metabolism
- chemical and physical activity



Novel speciation alternative – SPE-HG-AAS

μ-wave extraction → Separation by SPE → Detection by HG-AAS

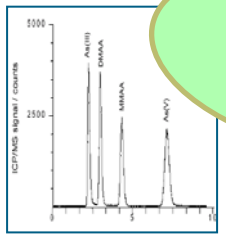
Example As speciation

The analytical speciation workhorse – HPLC-ICPMS


HPLC (GC)


Column


ICPMS


Chromatogram

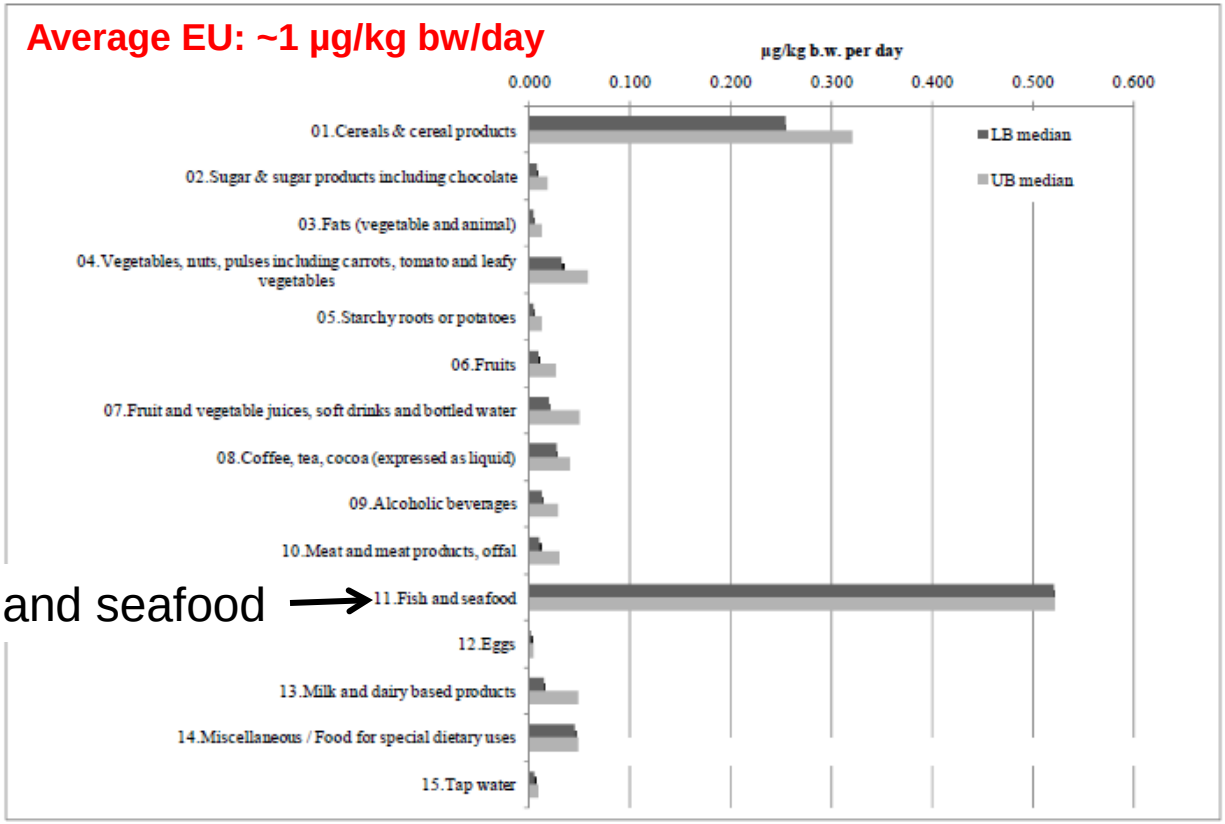
Example Hg speciation

Selected sample types

- Focus on marine feed and seafood

Seafood is the main dietary source of **arsenic** and mercury

Average EU: ~1 µg/kg bw/day



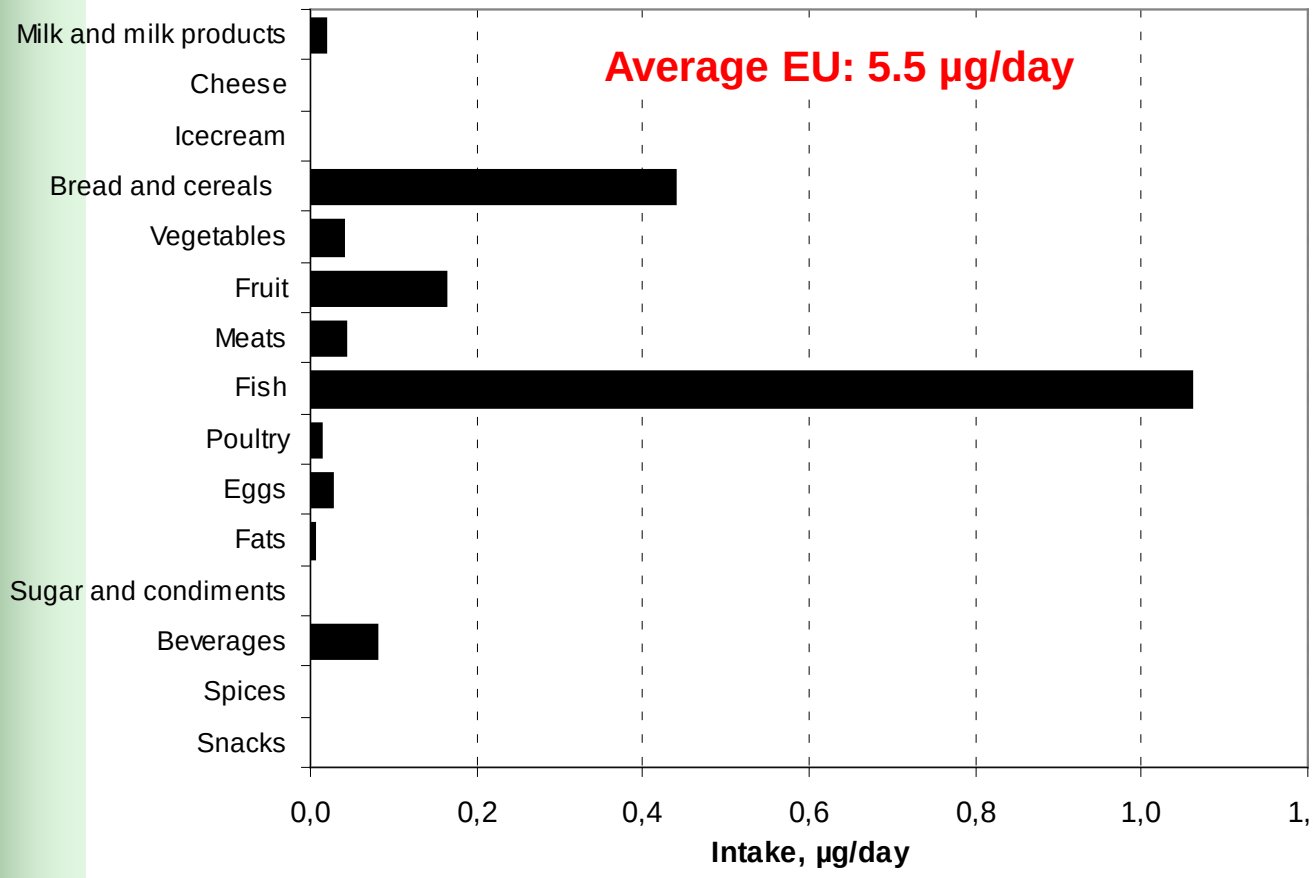
Fish and seafood →

EFSA (2009), Scientific Opinion on Arsenic in Food

Selected sample types

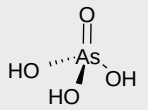
- Focus on marine feed and seafood

Seafood is the main dietary source of arsenic and **mercury**

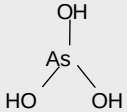


Ref: Danish Food Adm, 2004.

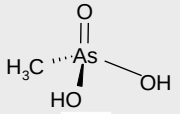
Arsenic compounds in the marine environment



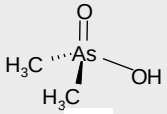
As(V)



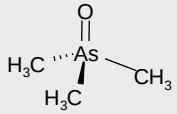
As(III)



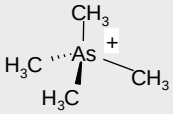
MA



DMA



TMAO



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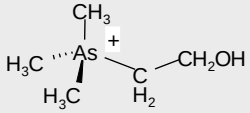
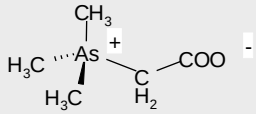
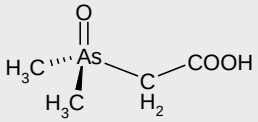


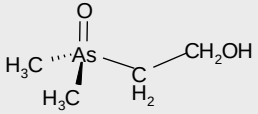
AC



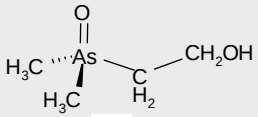
AB



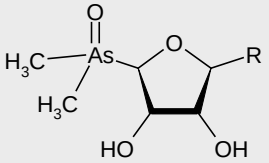
DMAA



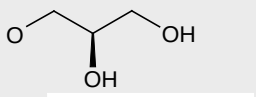
DMAE



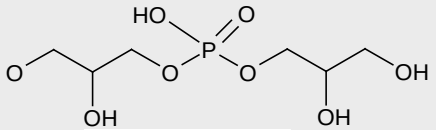
TMAP



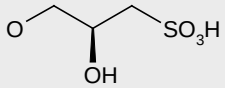
Dimethylarsinoylriboside



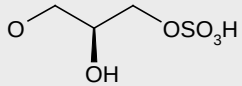
Dimethyl As-sugar 1



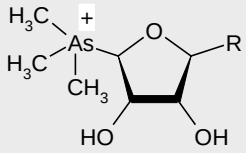
Dimethyl As-sugar 2



Dimethyl As-sugar 3



Dimethyl As-sugar 4

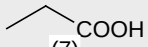


Trimethylarsonioriboside

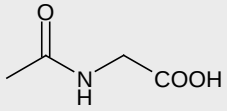
R = 1,2,3,4,5

OMe
(5)

H
(6)



(7)



(8)

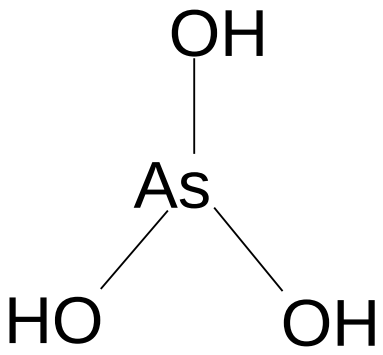
More than **50** different arsenic species have been found in the marine environment

Arsenic compounds in the marine environment

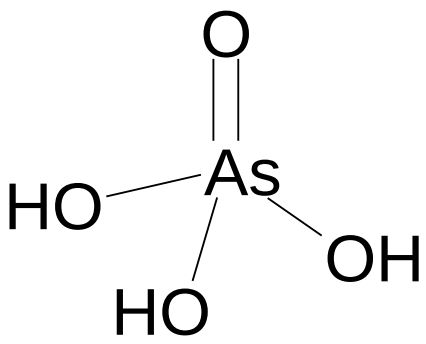
Arsenocosis

Most toxic form of arsenic!!

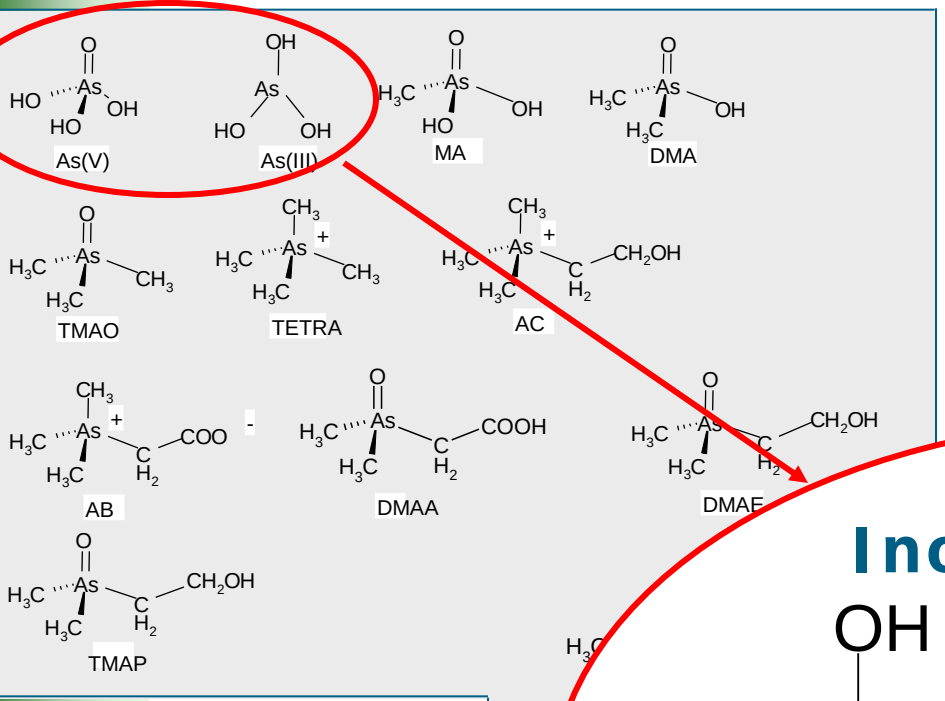
Inorganic arsenic

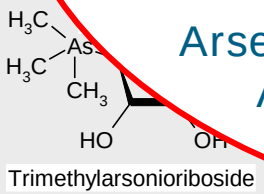


Arsenous acid
As(III)



Arsenic acid
As(V)

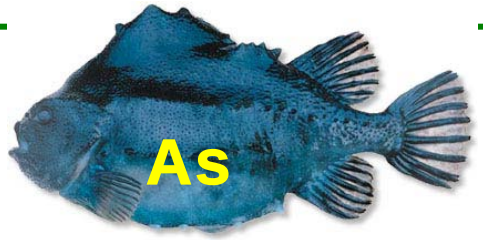




Trimethylarsonioriboside

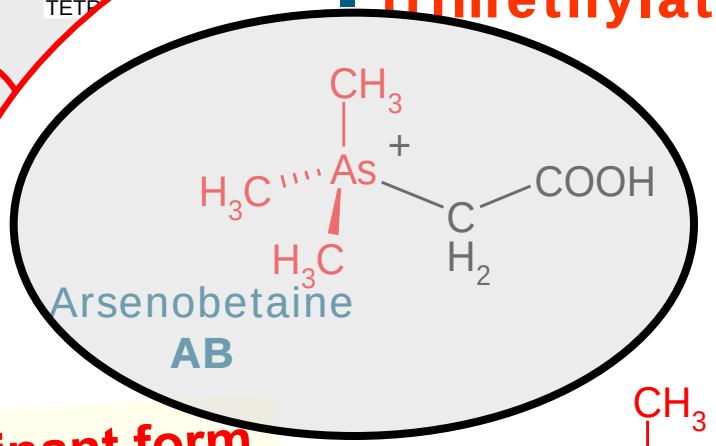
Focus on Food Safety

Arsenic compounds in the marine environment

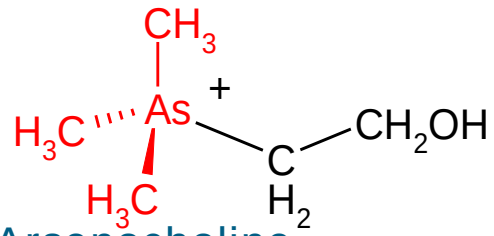


AB=”fish arsenic”
(Chapman, Analyst, 1920)

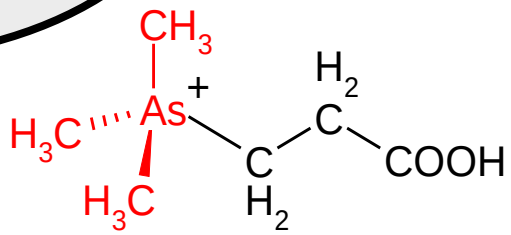
Organoarsenic compounds - trimethylated species



Arsenobetaine
AB



Arsenocholine
AC



Trimethylarsoniopropionic acid
TMAP

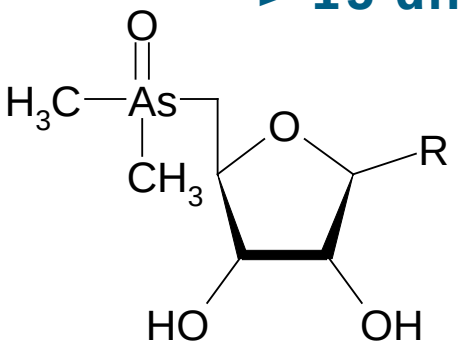
Predominant form of arsenic in most seafood!!

Arsenic compounds in the marine environment

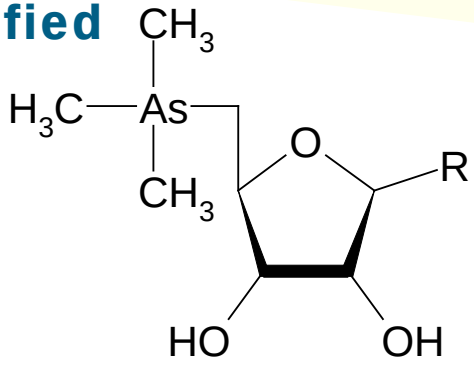
Arsenosugars

> 15 different identified

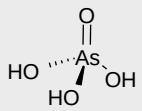
Predominant form of arsenic in algae!!



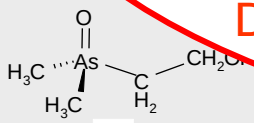
Dimethylarsinoylribosides



Trimethylarsonioribosides



As(V)



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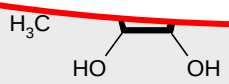
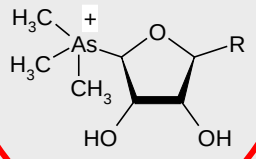


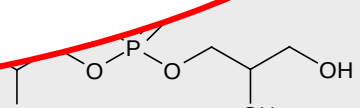
Dimethylarsinoylriboside



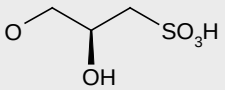
Trimethylarsonioriboside

R = 1,2,3,4,5

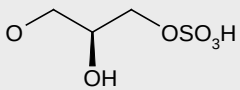
Dimethyl As-sugar 1



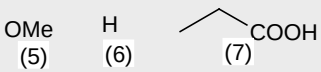
Dimethyl As-sugar 2

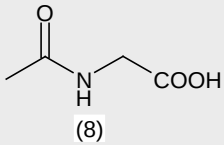


Dimethyl As-sugar 3



Dimethyl As-sugar 4





Commission directive 2009/114/EC (amendment)

Undesirable substances	Products intended for animal feed	Maximum content in mg/kg (ppm) relative to a feedingstuff with a moisture content of 12 %
(1)	(2)	(3)
'1. Arsenic (*) (**)	Feed materials with the exception of:	2
	— meal made from grass, from dried lucerne and from dried clover, and dried sugar beet pulp and dried molasses sugar beet pulp,	4
	— palm kernel expeller,	4 (***)
	— phosphates and calcareous marine algae,	10
	— calcium carbonate,	15
	— magnesium oxide,	20
	— feedingstuffs obtained from the processing of fish or other marine animals, including fish,	25 (***)
	— seaweed meal and feed materials derived from seaweed,	40 (***)
	Iron particles used as tracer.	50
	Additives belonging to the functional group of compounds of trace elements except:	30
	— zinc oxide, manganese oxide and copper oxide,	100
	Complete feedingstuffs with the exception of:	2
	— complete feedingstuffs for fish and complete feedingstuffs for fur animals,	10 (***)
	Complementary feedingstuffs with the exception of:	4
	— mineral feedingstuffs,	12

Only max levels for total arsenic!!

FOOTNOTE

(***) Upon request of the competent authorities, the responsible operator must perform an analysis to demonstrate that the content of **Inorganic arsenic lower than 2 ppm** s of particul… seaweed species *Hizikia fusiforme*.'

Speciation analysis is required !!

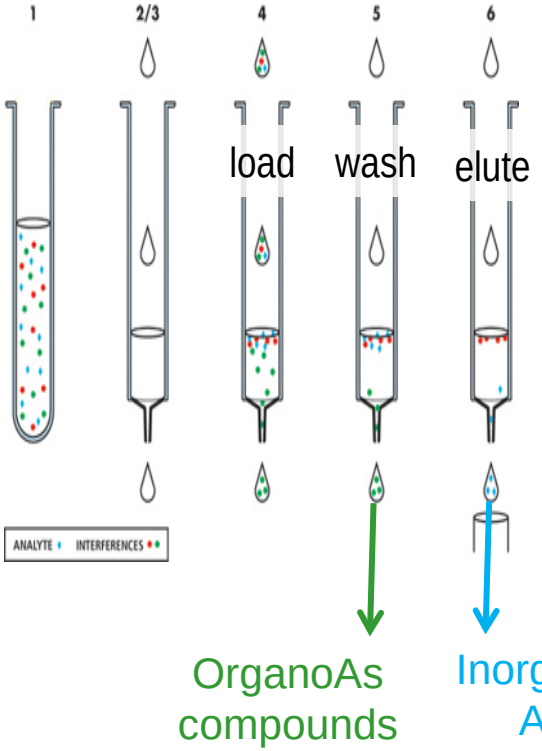
SPE-HG-AAS – a novel speciation alternative…

μ-wave extraction

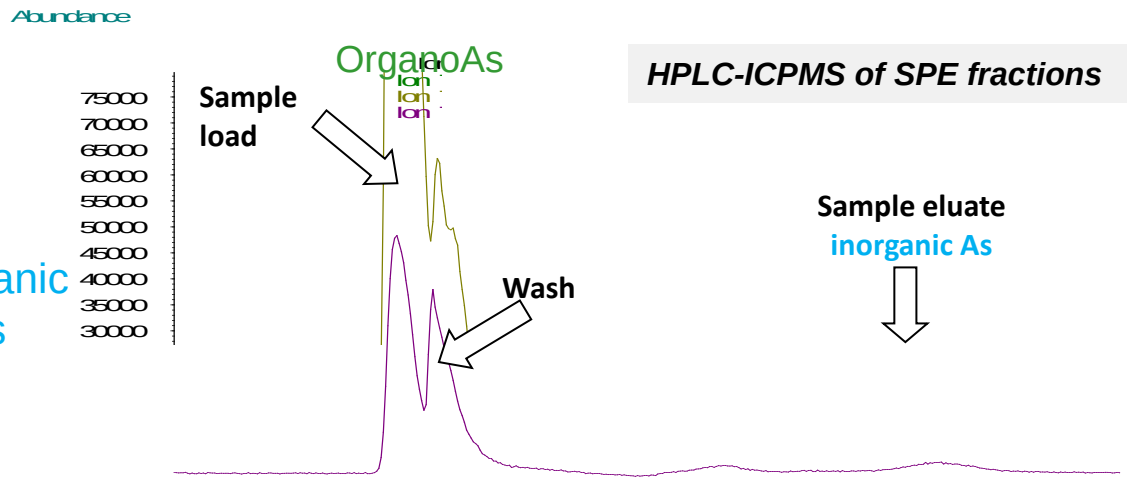
Separation by SPE

Detection by HG-AAS

Inexpensive detection system



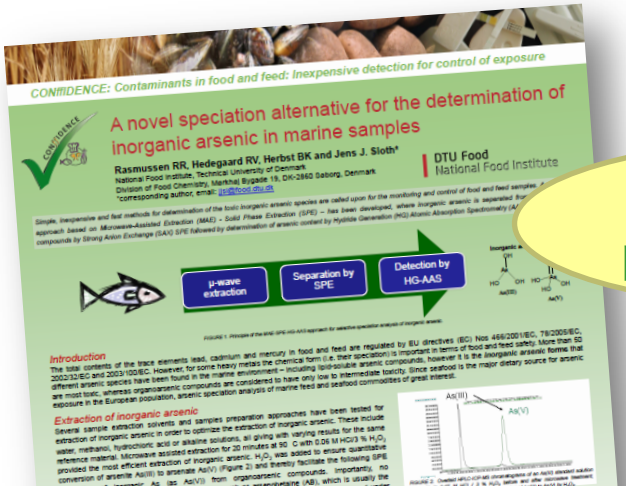
Sequential elution for selective off-line separation of inorg As from organo As species by SPE



HPLC-ICPMS of SPE fractions

Performance characteristics from in-house validation

Parameter	Result
Analysis time	2 x 7 h for 24 samples
LoD (mg/kg)	0.08
LoQ (mg/kg)	0.16
Repeatability (%RSD)	3 - 7
Accuracy (%)	90 - 104


CONfIDENCE: Contaminants in food and feed: Inexpensive detection for control of exposure

A novel speciation alternative for the determination of inorganic arsenic in marine samples

Rasmussen RR, Hedegaard RV, Herbst BK and Jens J. Sloth*

DTU Food National Food Institute

Further details on poster and handouts

EFSA (2009) and JECFA (2010) opinions on arsenic in food

- Old PTWI value (WHO, 1988) was withdrawn

- **NEW!** $BMDL_{1.0}$ = 0.3 – 8 µg/kg bw per day for inorganic arsenic
- => EU dietary exposures within this range
- => Risk to some consumers cannot be excluded

- **NEW!** $BMDL_{0.5}$ = **3 µg/kg bw per day** for inorganic arsenic
  => *0.5% increased incidence of lung cancer for 12 y exposure*

- *"…more accurate information on the inorganic arsenic content of foods is needed to improve assessments of dietary exposures to inorganic arsenic"*

- *"…need for validated methods for selective determination of inorganic arsenic in food matrices"*

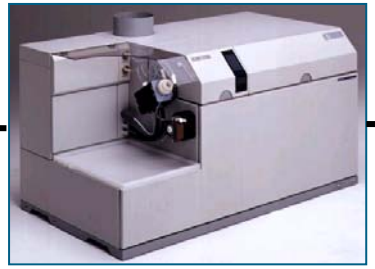
Speciation analysis of Mercury by HPLC-ICPMS

High capacity!

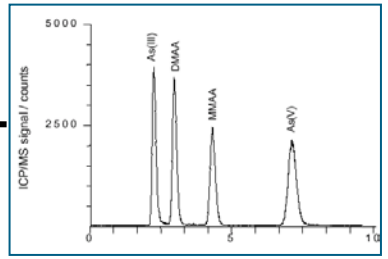
Ultra-sonification

HPLC

Column



ICPMS

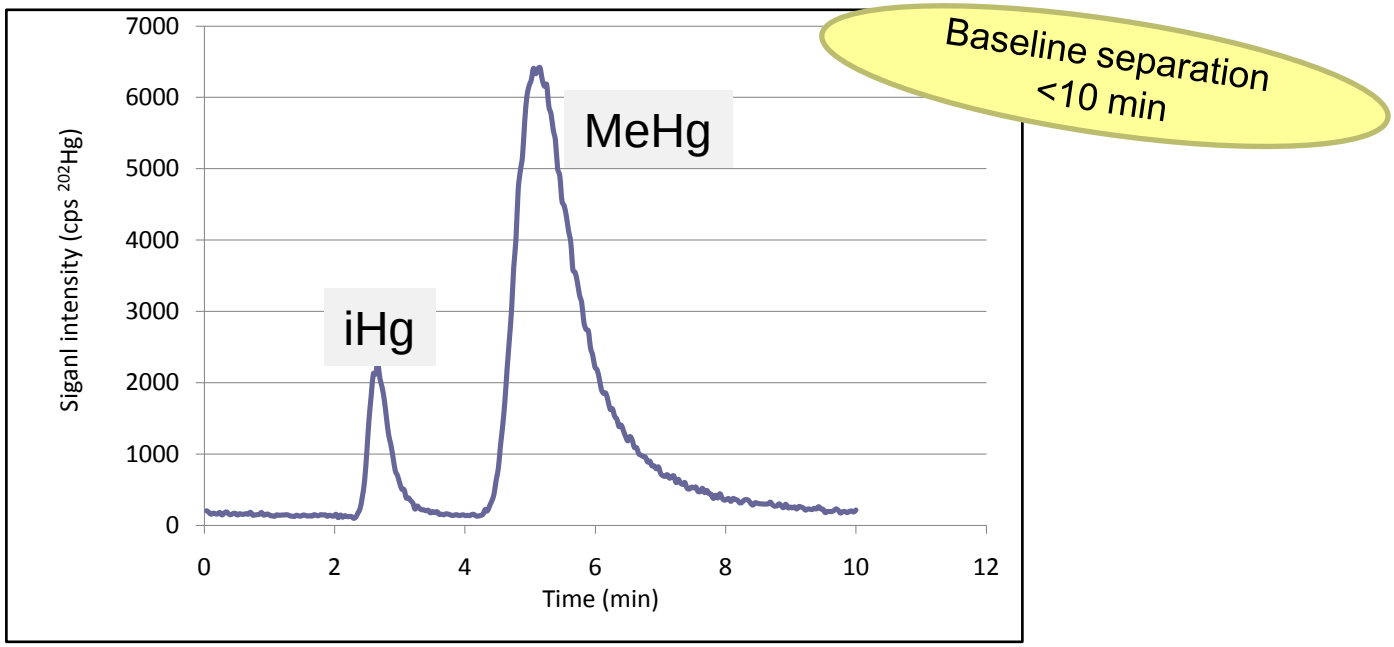


Result

MeHg is a priority contaminant

- Adverse effects on the central nerveous system
- Affects the learning ability of children
- Bioaccumulation and biomagnification in the aquatic food chain
- Biomethylation in the food chain: iHg -> MeHg
- Toxicity: MeHg > inorganic Hg
- PTWI MeHg: 1.6 µg/kg bw/week

Speciation analysis of Mercury by HPLC-ICPMS



HPLC-ICPMS chromatogram of DORM-3 (Dogfish muscle)

CRM	Certified (mg/kg)	Result (mg/kg)
DORM-2 (dogfish muscle)	4.47 +/- 0.32	4.21
DORM-3 (dogfish muscle)	0.355 +/- 0.056	0.35
TORT-2 (Lobster hepatopancreas)	0.152 +/- 0.013	0.16

Conclusion

- Total concentration info – not always sufficient!
- Speciation analysis for improved risk assessment
- Need for speciation methods for future monitoring
- ....and in feed and food control

Thanks for your attention!

Further information:

Speciation – chemical analysis: jjsl@food.dtu.dk **(Jens J. Sloth)**

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Miscalleneous **info on speciation**: EVISA homepage; www.speciation.net

evisa.

Further developments in **CONffIDENCE**: www.conffidence.eu

CONffIDENCE